

Third-order nonlinear optical interactions of C₆₀ and C₇₀

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We measured the third-order nonlinear optical susceptibility $\chi^{(3)}$ for C₆₀ and C₇₀ solutions as a function of concentration using degenerate four-wave mixing with picosecond pulses at 532 nm. From the observed minimum we were able to obtain the real and imaginary parts of $\chi^{(3)}$. The real part is negative at this wavelength. Values of the real and imaginary components of the molecular hyperpolarizability (γ) calculated are in the range 10^{-31} esu.

Conjugated polymers are receiving much attention in nonlinear optics¹ in view of potential applications. Buckminsterfullerenes are similar materials containing highly delocalized electrons and so are also interesting candidates in view of their expected high nonlinearity. Blau *et al.*² studied degenerate four-wave mixing (DFWM) in benzene solutions of C₆₀ with 50 ps pulses at 1.064 μ m. The high values of third-order nonlinearity they reported are contradicted by Knize and Partanen³ and Kafafi *et al.*^{4,5} Hoshi *et al.*⁶ studied optical second- and third-harmonic generation in C₆₀ films using a Nd:YAG laser as the fundamental source. Kafafi *et al.*⁵ reported values of third-order susceptibility $\chi_{XXXX}^{(3)}$ and molecular second hyperpolarizability γ for C₆₀ films using DFWM at 1.064 μ m with Nd:YAG laser picosecond pulses. Talapatra *et al.*⁷ theoretically calculated the molecular second hyperpolarizability of C₆₀ by the time-dependent coupled-perturbed Hartree-Fock approach. They measured γ of C₆₀ in benzene solution using techniques of DFWM at 602 nm and optical Kerr gate at 620 nm with femtosecond pulses. Zhang *et al.*⁸ studied third-order nonlinearities of C₆₀ and C₇₀ using time delayed DFWM with 30 ps pulses at 532 nm. In their measurements of $\chi^{(3)}$ versus concentration in toluene solutions, though they observed a minimum for C₇₀, they were not able to obtain the real and imaginary components. They could not observe the minimum of $\chi^{(3)}$ for C₆₀ solutions perhaps due to lack of more detailed data in the low concentration regime.

In this communication we report experimental measurements of the third-order nonlinear optical susceptibility $\chi^{(3)}$ for C₆₀ and C₇₀ solutions in several solvents as a function of concentration. From the observed minimum we were able to obtain the real and imaginary parts. The C₆₀ and C₇₀ purchased from Materials Electrochemical Research Corporation are quoted to be at least 99% pure. The optical absorption spectra are shown in Fig. 1. Values of $\chi^{(3)}$ are measured using the technique of DFWM at 532

nm with 25 ps pulses obtained from a frequency doubled Nd:YAG laser. The vertically polarized output is split into three beams, which are temporally and spatially overlapped in the sample contained in 2 mm cuvettes. Full details of the experimental technique are described in an earlier publication.⁹ Following standard procedure, $\chi^{(3)}$ values for the solvents are obtained by comparison with measurements on a reference sample CS₂ of the same length under identical conditions. In the case of C₆₀, C₇₀ solutions, the solvent itself is used as the reference. The phase conjugate signal studied as a function of incident intensity showed the cubic dependence characteristic of a third-order process for the intensities (maximum of 0.1 GW/cm²) and the low concentrations used in the experiment.

The second hyperpolarizability $\langle\gamma\rangle$ of a molecule in isotropic media is related¹ to third-order macroscopic susceptibility by the equation

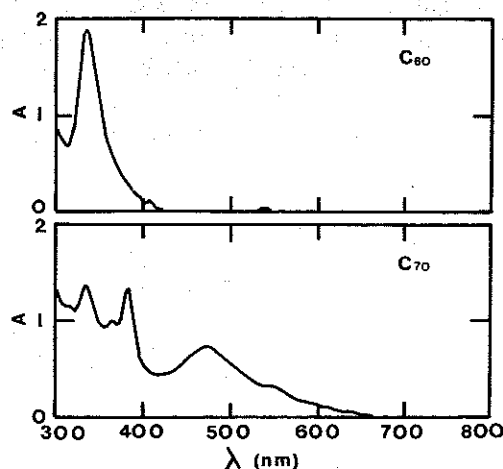


FIG. 1. Optical absorption spectrum for 10×10^{-5} g/ml solutions of C₆₀ and C₇₀ in toluene, 99% pure.

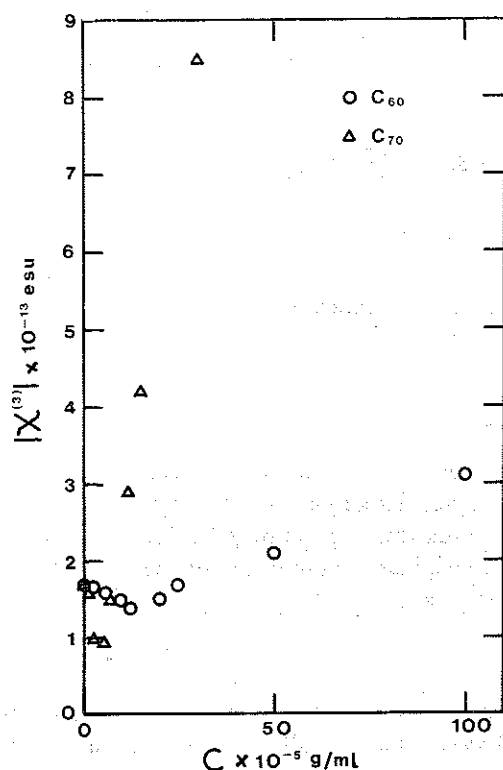


FIG. 2. Concentration dependence of $|\chi_{\text{solution}}^{(3)}|$ of C_{60} and C_{70} in toluene.

$$\langle \gamma \rangle = \frac{\chi^{(3)}}{L^4 N}, \quad (1)$$

where N is the number density of molecules cm^{-3} . L is the local field correction factor given by $(n^2 + 2)/3$, where n is the index of refraction. For dilute solutions of noninteracting particles assuming a pairwise additive model,⁹ we may write

$$\chi_{\text{solution}}^{(3)} = L^4 (N_{\text{solvent}} \gamma_{\text{solvent}} + N_{\text{solute}} \gamma_{\text{solute}}), \quad (2)$$

where N_{solvent} , N_{solute} are the number densities of molecules of the solvent and solute.

In general $\chi^{(3)}$ and γ are complex and consist of the real and imaginary components for both solute and solvent. The real part, which can be either positive or negative contributes to the nonlinear refractive index while the imaginary part is responsible for nonlinear absorption. In the case of most organic solvents, which are transparent in

the visible region of the spectrum, we assume the imaginary component to be zero as was also done by Talapatra *et al.*⁷ So we have

$$|\chi_{\text{solution}}^{(3)}| = L^4 [(N_{\text{solvent}} \gamma'_{\text{solvent}} + N_{\text{solute}} \gamma'_{\text{solute}})^2 + (N_{\text{solute}} \gamma''_{\text{solute}})^2]^{1/2}. \quad (3)$$

If $N_{\text{solvent}} \gamma'_{\text{solvent}} = -N_{\text{solute}} \gamma'_{\text{solute}}$ (the contribution of the real parts due to solute and solvent cancel each other), $|\chi_{\text{solution}}^{(3)}|$ has a minimum value given by

$$|\chi_{\text{solution}}^{(3)}|_{\text{min}} = L^4 N_{\text{solute}} \gamma''_{\text{solute}} = |\text{Im } \chi_{\text{solution}}^{(3)}|. \quad (4)$$

For an interesting case of this type we can obtain both $\text{Re } \chi_{\text{solution}}^{(3)}$ and $\text{Im } \chi_{\text{solution}}^{(3)}$ from the observed minimum in the plot of $\chi_{\text{solution}}^{(3)}$ versus concentration.

The results are illustrated in Fig. 2 for C_{60} and C_{70} solutions in toluene. Values of real and imaginary parts of $\chi_{\text{solution}}^{(3)}$ for the appropriate concentration where the minimum is observed are listed in Table I. The real and imaginary components of $\langle \gamma \rangle$ obtained from these values are also shown in the table. The experiments for C_{60} are repeated with different solvents and the results are also listed in the table.

It may be seen from the table that the values of $\langle \gamma' \rangle$ and $\langle \gamma'' \rangle$ obtained from measurements on different solvents for C_{60} are in approximate agreement. The real components of C_{60} and C_{70} are negative at this wavelength (assuming $\chi_{\text{solvent}}^{(3)} > 0$). The sign is an important parameter for many nonlinear optical applications.

Considering the wavelengths at which the experiments are carried out, our values of $\langle \gamma \rangle$ for C_{60} are in line with Talapatra *et al.*⁷ and Kafafi *et al.*⁵ Kafafi *et al.* reported γ for C_{60} thin films as 3×10^{-34} esu at the off-resonant wavelength 1.064 μm . Talapatra *et al.*'s values at 602 nm wavelength for γ' of -5×10^{-33} esu and γ'' of 9×10^{-33} esu are larger, perhaps due to resonant enhancement. Our values for C_{60} at 532 nm are even greater for the same reason as we are approaching the absorption peak.

Zhang *et al.*'s⁸ value of γ_{1212} for C_{60} at 532 nm of 1.6×10^{-29} esu is approximately two orders larger than our value. Similarly, their value for C_{70} of 6.0×10^{-27} is about three orders larger than our value. If we consider the difference in their polarization scheme, the disagreement is even more. Looking at the linear absorption coefficient α , we find their value for C_{60} solution about seven times larger and for C_{70} about 20 times larger compared to our values

TABLE I. Values of real and imaginary parts of third-order susceptibility and second hyperpolarizability for C_{60} and C_{70} .

Solute	Solvent	Concentration	Re $\chi_{\text{solution}}^{(3)}$ at min. (10^{-13} esu)	Im $\chi_{\text{solution}}^{(3)}$ at min. (10^{-13} esu)	$\langle \gamma' \rangle$ (10^{-31} esu)	$\langle \gamma'' \rangle$ (10^{-31} esu)
		for min. $ \chi_{\text{solution}}^{(3)} $ (10^{-5} g/ml)				
C_{60}	toluene	12.5	-1.7	1.4	-4.0	3.3
C_{60}	benzene	10.3	-1.4	1.2	-3.9	3.5
C_{60}	styrene	12.0	-1.6	1.2	-3.4	2.9
C_{60}	xylene	11.0	-1.1	0.8	-3.0	2.2
C_{70}	toluene	4.6	-1.7	0.9	-13.0	7.3

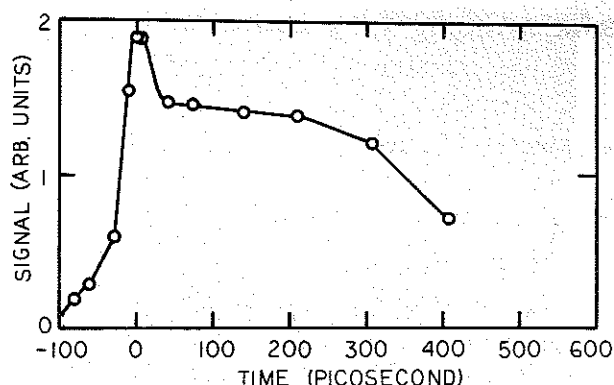


FIG. 3. Time dependence of the degenerate four-wave mixing signal of a 2.53×10^{-3} g/ml solution of C_{60} in toluene. All four beam waves have the same polarization.

for approximately the same concentrations. (Our values for α are $\alpha = 1.16 \text{ cm}^{-1}$ for a 0.25 mg/ml concentration of C_{60} in toluene, $\alpha = 1.25 \text{ cm}^{-1}$ for a 0.035 mg/ml concentration of C_{70} in toluene.)

For a solution with a concentration of 0.33 mg/ml we obtain a figure of merit $\chi^{(3)}/\alpha$ of 2.9×10^{-13} for C_{60} and 2.0×10^{-13} esu cm for C_{70} . The value obtained for a C_{60} thin film sample, approximately 10^{-12} , by Kafafi *et al.*⁵ is appreciably larger, although their measurements are at the off-resonant wavelength $1.064 \mu\text{m}$.

Time resolved measurements of the phase conjugate signal with all four beams of the same polarization for both C_{60} and C_{70} indicate a slow component with decay time much longer than picoseconds. The time evolution of the phase conjugate signal for a 2.53 mg/ml solution of C_{60} in toluene is shown in Fig. 3 as a function of backward pump delay for the case of all beams with the same polarization. The results indicate a decay time longer than 400 ps, which is the maximum delay that can be introduced in our experimental setup. Our observations of the time response of the phase conjugate signal for crossed polarization of the backward pump are similar to the previous case (except

for the magnitude of the signal, which is about a third compared to the signal for all four beams with the same polarization), indicating approximately the same decay time for the slow component. The results are consistent with the interpretation of the existence of a transient population grating probably due to an excited state.⁵ It may be mentioned that a value of about 650 ps for the decay time of the singlet state is reported by Sension *et al.*¹⁰ from a study of transient absorption spectra of similar fullerene solutions. More detailed studies are in progress to delineate the origin of the optical nonlinearities.

In conclusion, we employed a simple method of obtaining the real and imaginary parts of the molecular second hyperpolarizability $\langle\gamma\rangle$ for C_{60} and C_{70} from solution measurements of $\chi^{(3)}$ as a function of concentration. The real component is found to be negative at 532 nm wavelength.

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